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(54) Title: BRIQUETTING OF MINERAL FINES

(57) Abstract

Mineral fines such as coal fines are agglomerated structures into briquettes or tablets by a cold roll-press operation using as a binder an ester-cured alkaline phenol-formaldehyde resole resin together with an oxyanion to enhance green strength.

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BRIQUETTING OF MINERAL FINES

This invention relates to the briquetting of mineral fines such as coal fines.

A variety of techniques are known for producing agglomerated structures such as briquettes or tablets from coal fines. The most popular method is to form ovoid shapes by a cold roll-press operation. In this instance, the coal fines mixed with a binder are squeezed, at pressures of up to about 2.1×10^6 kg/m^2) (3000 psi), between two metal rolls each having half-ovoid depressions. The briquettes so formed fall from the press on to a conveyor belt for transfer to storage and subsequent packaging.

Several types of binder have been used in this process with varying degrees of success. For example, sodium silicate gives moderately strong briquettes, but has poor water resistance and because of increased ash content reduces the fuel value of the coal. Binders such as bitumen and sulphite lye result in the emission of fumes and smoke from the burning briquette which is clearly undesirable.

The use of ester-cured alkaline phenol-formaldehyde resole resin is known to give moderately strong briquettes with good burning properties and US Patent No. 4802890 is an example. However, a green strength additive, commonly a starch, must be used to provide very early strength so that the freshly formed ovoid can fall intact to the conveyer belt. Starch is susceptible to bacterial/fungal attack and therefore must be used with a biocide or fungicide. Furthermore, the inclusion of starch can detract from the strength achievable from the phenolic resin. From the mechanics of the operation, this system is also

complex because of the need for four components.

There is therefore a need for a binder for coal fines which substantially avoids these disadvantages. In addition the problem is not confined to coal fines since there is also a need to agglomerate fines of a variety of minerals whether in the form of particles or fibres.

According to the invention in one aspect an ambient temperature curing binder, for agglomerating mineral fines, comprises an alkaline resole phenol-formaldehyde resin, an ester co-reactant and an oxyanion to enhance green strength.

Also according to the invention there is provided a method of agglomerating a mineral fine in which the fine is bound into larger agglomerates by a binder comprising an alkaline phenol-formaldehyde, an ester co-reactant and an oxyanion to enhance green strength.

Thus, we have found that the inclusion of certain oxyanions, borate in particular, as a third component rapidly increases the viscosity of the resin-ester mixture and thus enhances the green strength of the system. This permits the briquette to fall intact onto a conveyer belt. The rapid increase in viscosity is believed to result from a decrease in pH of the resin coupled with ionic crosslinking between the methylol groups on the phenolic resin and the oxyanion. For example, the addition of 3% by weight of sodium tetraborate to the resin can give as much as a four-fold increase in viscosity.

The binder may be supplied as a briquetting binder system for binding mineral fines at ambient temperatures comprising as separate components:

(a) an alkaline resole phenol-formaldehyde resin;

(b) an ester co-reactant, and

(c) an oxyanion to enhance green strength of the resulting binder, to be mixed together with the mineral fines to form a mixture to be briquetted.

This system may have an indication that the resulting binder is useful for briquetting mineral fines such as coal. It may be supplied with the components in separate containers which may be of a relative size such that many of the contents of the containers with the fines will provide a resulting mixture where the components are in the desired relative proportions.

Unlike prior systems which include an organic material like starch, the briquettes resulting from the invention are not susceptible to mould and bacterial growth. Therefore, they do not need to include a bactericide or fungicide yet still remain bright and clear of mould on storage.

The alkaline resole phenol-formaldehyde resin may, for example, be one prepared by reacting a monohydric phenol such as phenol or a cresol, or a dihydric phenol such as resorcinol, with formaldehyde under alkaline conditions. The molar ratio of the monohydric or dihydric phenol to formaldehyde can be from 1:1 to 1:3, but the preferred range is 1:1.6 to 1:2.0. To this reactant mixture is added alkali as a solid or an aqueous solution. Hydroxides of calcium, sodium and potassium may be used, but the latter is preferred. The amount of solid alkali added can be from 8 to 18%, more preferably 12 to 18%, by weight of the resin, though the most preferred range is 11 to 15% by weight of the resin.

The ester co-reactant (curing agent) may, for example, be the acetic acid esters of ethylene glycol, propylene glycol, butylene glycol and glycerol, lactones such as propriolactone and gammabutyrolactone, and carbonate esters such as propylene carbonate and blends of ethylene/propylene carbonates. Mixtures of these esters may also be used.

Suitable oxyanions are borate, aluminate and stannate, although borate is preferred. Also the oxyanion can be present in the form of a salt such as the potassium or sodium salt.

The amount of alkaline phenol-formaldehyde resin to be added to the fines such as coal will normally be 1 to 6% by weight of the fines with the quantity of ester curing agent being 15 to 25% by weight based on the weight of resin. The oxyanion, which can conveniently be added as a 5% aqueous solution, will usually be added in an amount of 1 to 6% by weight based on the fines. These amounts are generally higher than the amounts which would be needed for larger sized particles than fines.

The preferred order of addition to the mineral fines is to add the oxyanion first, then the ester and finally the resin, allowing time between each addition to disperse the component in the mixture.

The binding will take place at ambient temperatures and so no separate heating of the components is required. Thus, in the case of the briquetting of coal fines little or no change is required to the cold roll-press operation other than the use of a binder according to the invention in place of traditional binders such as sodium silicate and normally the coal fines will be in the form of a damp mixture to avoid dust problems.

Besides coal fines the agglomeration process of the invention can be used with other types of fines such as carbon and graphite, and with other minerals such as quartz, calcium silicate and alumino-silicate. Mixtures of fines such as mixtures of various carbon based fines and silica fines are also possible.

The coal and other fines will normally have a maximum size of such that they will pass a mesh of 5 millimetre square aperture, and preferably a mesh of 3 millimetre square aperture. The fines will therefore contain a range of particle sizes up to the maximum noted above. More preferably the fines are of a maximum size range of from 150 to 200 mesh.

In some circumstances it may also be desirable to add a silane to assist in bonding between the binder and the mineral and a particular example is quartz. The silane, if present, is preferably added in an amount of from 0.1 to 1.0% by weight of the resin.

The invention can be illustrated by the following Example.

A resole phenol-formaldehyde resin was prepared by reacting, under mild alkaline conditions, 450 g of phenol and 270 g of 91% paraformaldehyde in the presence of 351 g of water for 15 minutes at 100 C. After cooling to 80 C, 93 g of potassium hydroxide (45% w/w aqueous solution) was added and the reaction continued at 80 C until the viscosity had increased to 17A (The Paint Research Association Bubble Tube @ 25 C). After cooling the reaction mass, 325 g of potassium hydroxide (45% w/w aqueous solution) were added. Finally, 4 g of gamma-aminopropyltriethoxy silane were added. The finished resin had a viscosity of 350 centipoise (Brookfield ERV-8 @ 20 C/Spindle 4/100 rpm) and a

solids content of 53% (3h @ 120C).

A coal fines mixture comprising 70% anthracite, 20% petrocoke and 10% bituminous with an overall moisture content of 8.5% were mixed with 3% by weight of a 5% aqueous solution of sodium tetraborate followed by 1% by weight of an ester comprising equal parts of triacetin and gamma-butyrolactone. The resin as prepared above was then added at 4% by weight based on the fines and dispersed for 1 minute.

This mixture was formed into briquettes by the roll-press technique, the ovoids so formed remaining intact on falling from the press. Green strength measurement within 30 seconds from forming gave values of about 2.46×10^4 to 3.16×10^4 kg/m^2 (35 to 45 psi). After 24 hours the briquettes had good scratch hardness, the compression strength had increased to about 9.84×10^4 to 1.12×10^5 kg/m^2 (140 to 160 psi) and immersion tests showed them to be water resistant. Burn tests showed the briquettes to have excellent hot strength and to evolve very little smoke or fumes.

The above briquetting exercise was repeated with the 5% aqueous solution of sodium tetraborate replaced, on a weight-weight basis, by 3% of water alone. Over 70% of the ovoids disintegrated on falling from the roll-press, showing little evidence of any measurable green strength.

CLAIMS:

1. A ambient temperature curing binder for agglomerating mineral fines comprising an alkaline resole phenol-formaldehyde resin, an ester co-reactant and an oxyanion to enhance green strength.

2. A briquetting binder system for binding mineral fines at ambient temperatures comprising as separate components:

(a) an alkaline resole phenol-formaldehyde resin;

(b) an ester co-reactant, and

(c) an oxyanion to enhance green strength of the resulting binder, to be mixed together with the mineral fines to form a mixture to be briquetted.

3. A binder as claimed in Claim 1 or a system as claimed in Claim 2 in which the resin is one which has been formed by reacting a monohydric or dihydric phenol with formaldehyde under alkaline conditions and in which the molar rates of the monohydric or dihydric phenol to formaldehyde is preferably 1:1 to 1:3.

4. A binder or system as claimed in Claim 3 in which calcium, sodium or potassium hydroxide provided the alkaline conditions and was present in an amount of from 8 to 18% by weight of the resin.

5. A binder or system as claimed in any preceding claim in which the ester co-reactant is an acetic acid ester, a lactone or a carbonate ester, and in which the quantity of ester co-reactant is preferably from 15 to 25% by weight of the weight of the resin.

6. A binder or system as claimed in any preceding claim in

which the oxyanion is a borate, aluminate or stannate.

7. A binder as claimed in any preceding claim which additionally includes a silane preferably in an amount of from 0.1 to 1.0% by weight of the resin.

8. A method of agglomerating a mineral fine in which the fine is bound into larger agglomerates by a binder comprising an alkaline phenol-formaldehyde, an ester co-reactant, and an oxyanion to enhance green strength.

9. A method of agglomerating a mineral fine in which the fine is bound into larger agglomerates by a binder or system as claimed in any of claims 1 to 7.

10. A method as claimed in Claim 8 or Claim 9 in which the mineral is coal and the larger agglomerates are ovoid briquettes formed by a cold-press operation.

11. A method as claimed in any of claims 8 to 10 in which the resin is added to the fines in an amount of from 1 to 6% by weight of the fines and the oxyanion in an amount of from 0.05 to 0.3% by weight of the fines.

12. A method as claimed in any of claims 8 to 11 in which the oxyanion is added first to the fines, then the ester co-reactant and finally the resin, the component added being allowed to disperse into the mixture before the next component is added.

INTERNATIONAL SEARCH REPORT

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PCT/GB 96/02479

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C10L5/14 C10L5/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,4 802 890 (R.F. VILES) 7 February 1989 cited in the application see the whole document ---	1-12
Y	EP,A,0 323 096 (FOSECO INTERNATIONAL LIMITED) 5 July 1989 see claims 1-25 ---	1-12
A	GB,A,2 282 387 (HEPWORTH MINERALS & CHEMICALS LIMITED) 5 April 1995 see page 3, line 12 - line 15; claims 1-3 --- -/--	1-12

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 8419 Derwent Publications Ltd., London, GB; Class L02, AN 84-119072 XP002023245 & SU,A,1 033 255 (LIPETSK POLY) , 7 August 1983 see abstract ---	
A	GB,A,2 154 593 (FOSECO INTERNATIONAL LIMITED) 11 September 1985 -----	

INTERNATIONAL SEARCH REPORT

Internat[illegible]ision No
PCT/GB 96/02479

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-4802890	07-02-89	AU-B-	587115	03-08-89
		AU-A-	7053887	15-10-87
		CA-A-	1284029	14-05-91
		EP-A-	0241156	14-10-87
EP-A-323096	05-07-89	AU-A-	2660188	29-06-89
		CA-A-	1332256	04-10-94
		DE-A-	3873718	17-09-92
		FI-B-	97811	15-11-96
		IN-A-	172931	08-01-94
		JP-A-	1224263	07-09-89
		JP-C-	1789340	29-09-93
		JP-B-	4076947	07-12-92
		KR-B-	9312260	28-12-93
		US-A-	4977209	11-12-90
		US-A-	4985489	15-01-91
GB-A-2282387	05-04-95	NONE		
GB-A-2154593	11-09-85	AU-B-	575911	11-08-88
		AU-A-	3900285	05-09-85